

# UNDERSTANDING MERCURY OXIDATION AND ITS OPTIMIZATION FOR THE DEVELOPMENT OF MERCURY CONTROL TECHNOLOGIES

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Storch Award - Prof. Colin E. Snape

A recurring problem...



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Colin's first ACS meeting



# The mercury problem

- EPA has identified mercury as a hazardous air pollutant.
- Coal utility boilers are the largest source of anthropogenic mercury emissions (US-EPA study):
  - ~ 30 tons captured in ash and scrubber residues.
  - ~ 45 tons emitted to atmosphere.
- Mercury control regulations:
  - In US: Clean Air Mercury Rule (CAMR) and Clean Air Interstate Rule (CAIR), issued by EPA.
  - In Europe: 'Development of an EU mercury strategy'

# Mercury capture in existing APCDs



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- An enhanced utilization of the already existing APCDs is considered as a cost-effective approach compared to the development of new and mercury-specific removal technologies.
- A combination of existing wet FGD and selective catalytic reduction SCR with electrostatic precipitators (ESP) can reduce significantly emissions for bituminous coals.
- However, this combination of APCDs does not provide nearly as high reductions in Hg emissions for low-rank coals.
  - Overall mercury removal efficiency of APCDs mainly depends on the occurrence of mercury species and their properties.
  - Plants burning coals that emit mainly Hg(0) will face an even greater challenge in achieving a high level of control at acceptable cost.

# Mercury capture injecting activated carbons



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- Injection of commercial activated carbons is a promising technology.
- Barriers: low concentration of mercury (ppb), complexity of flue gas composition, short residual time of sorbent and poor selectivity:
  - Excess of carbon injected
- Novel sorbents are being developed.

# Mercury oxidation: Effect of fly ash components



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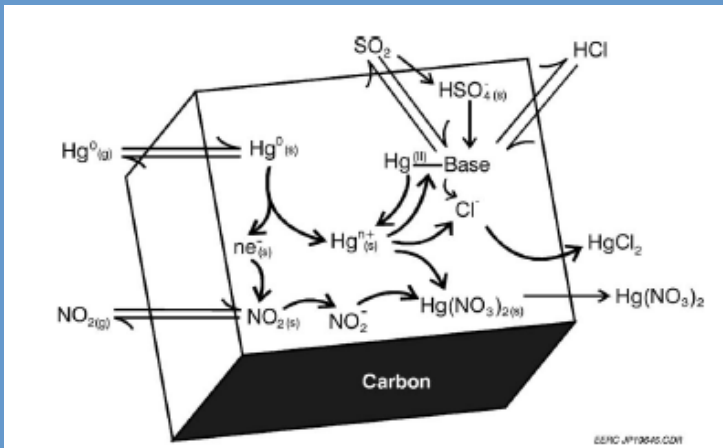
- Hg(0) shows little tendency to adsorb on sorbents or unburned carbon present in fly ash and is also insoluble in wet FGD units, although it can be adsorbed by brominated activated carbons.
- Hg (II) such as present in  $\text{HgCl}_2$  (g) is readily adsorbed on fly ash or dedicated sorbents at appropriate temperatures and could be almost totally retained in FGDs because of its high water solubility.
- Heterogeneous mercury oxidation occurs between mercury in flue gas and components of fly ash.

# Mercury oxidation: Effect of flue gas composition



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- Heterogeneous chemistry:
  - Testing in synthetic flue gas on Hg adsorption on activated carbon identified that the interaction between SO<sub>2</sub> and NO<sub>2</sub> severely impaired the capture of Hg, whereas HCl, NO, and NO<sub>2</sub>, either individually or combined, enhanced Hg capture.
  - In the presence of fly ash, NO<sub>2</sub>, HCl, and SO<sub>2</sub> have been found to promote Hg oxidation, primarily due to NO<sub>2</sub>, while NO had an inhibitory effect.
- Homogeneous chemistry:
  - Strongly influenced by the coal chlorine content, where Hg(0) reacts with atomic Cl to yield HgCl, followed by the oxidation of HgCl by Cl<sub>2</sub> to produce HgCl<sub>2</sub>.



Pavlish et al. *Fuel Proc. Tech.*, **2003**, 82,

# Research needs



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Colin's PhD award ceremony  
Leeds, August 1982



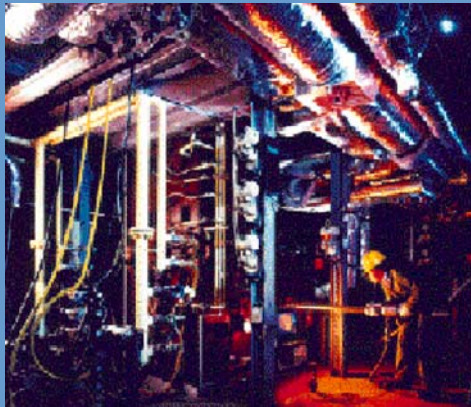
# Research needs-I



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The Nottingham Fuel and Energy Centre (NFEC) is currently involved in a series of national and international research projects to address the following issues in mercury research:



1. To evaluate the influence of flue gas composition, temperature, contact time on mercury species and concentration.

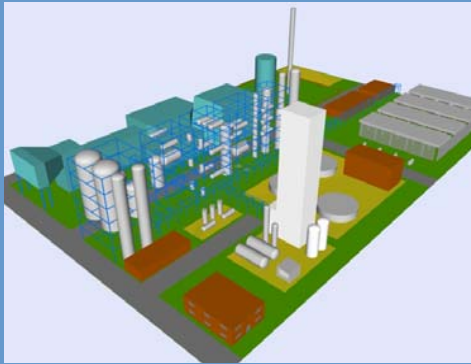


2. To determine the capacity of the different components of fly ashes (different types of unburned particles and mineral phases), for mercury retention.

# Research needs-II

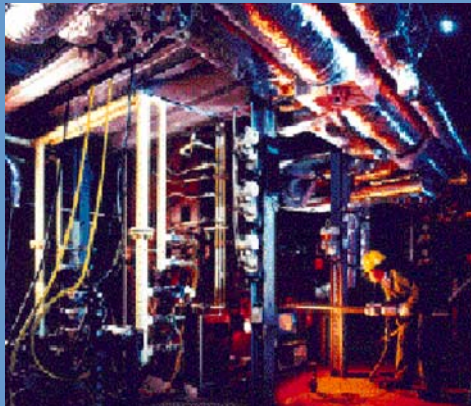


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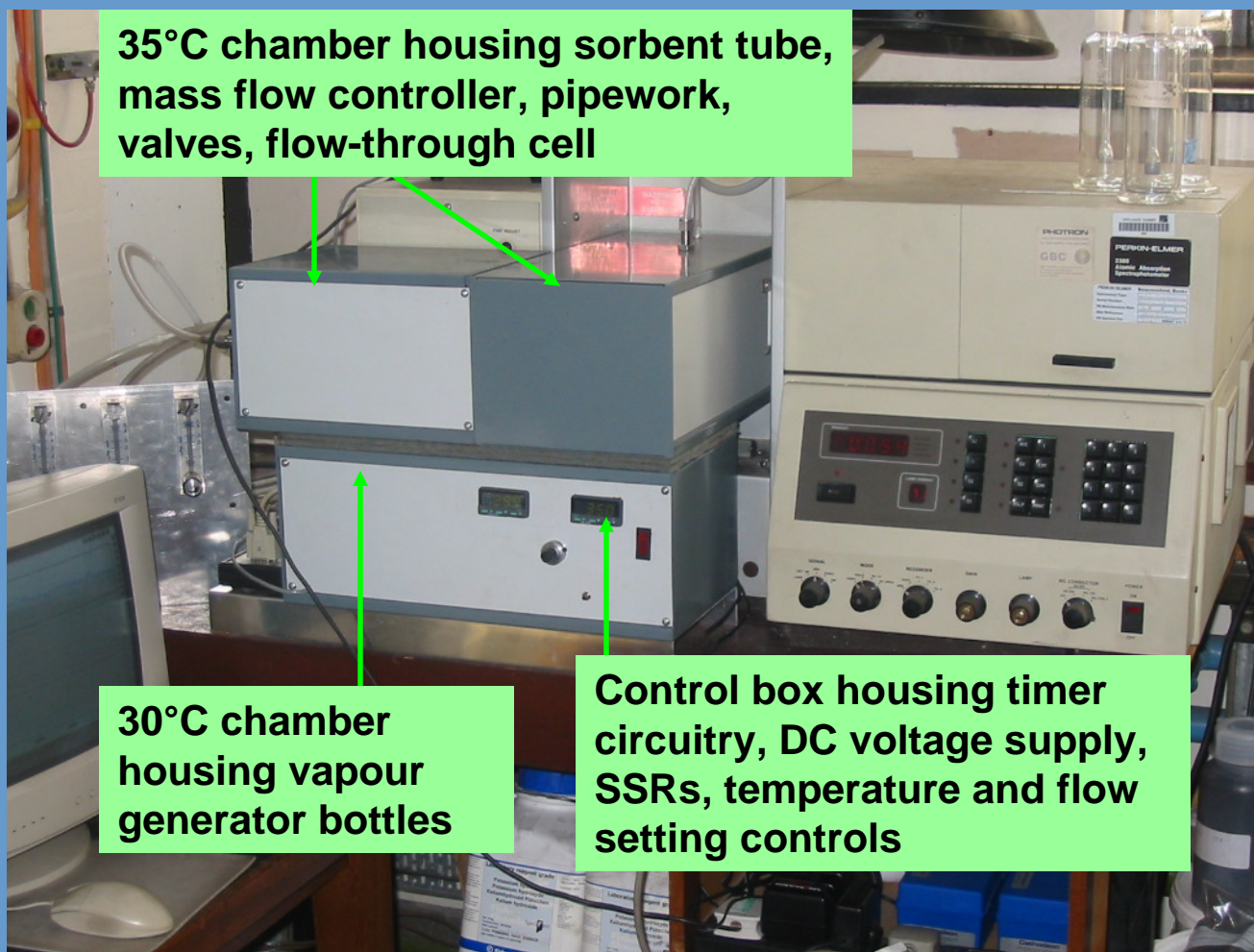
3. To identify the oxidation mechanisms of mercury on fly ashes.
4. To optimise ash composition, possibly aided by direct injection of individual ash components, to maximise the oxidation of  $\text{Hg}(0)$  to  $\text{Hg}(\text{II})$ .
5. To develop sorbents by: (i) conducting fundamental studies; and (ii) injection testing of the optimized sorbents to evaluate their performance under actual plant conditions



# Hg test facility for screening adsorbents



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# Hg test facility for screening adsorbents



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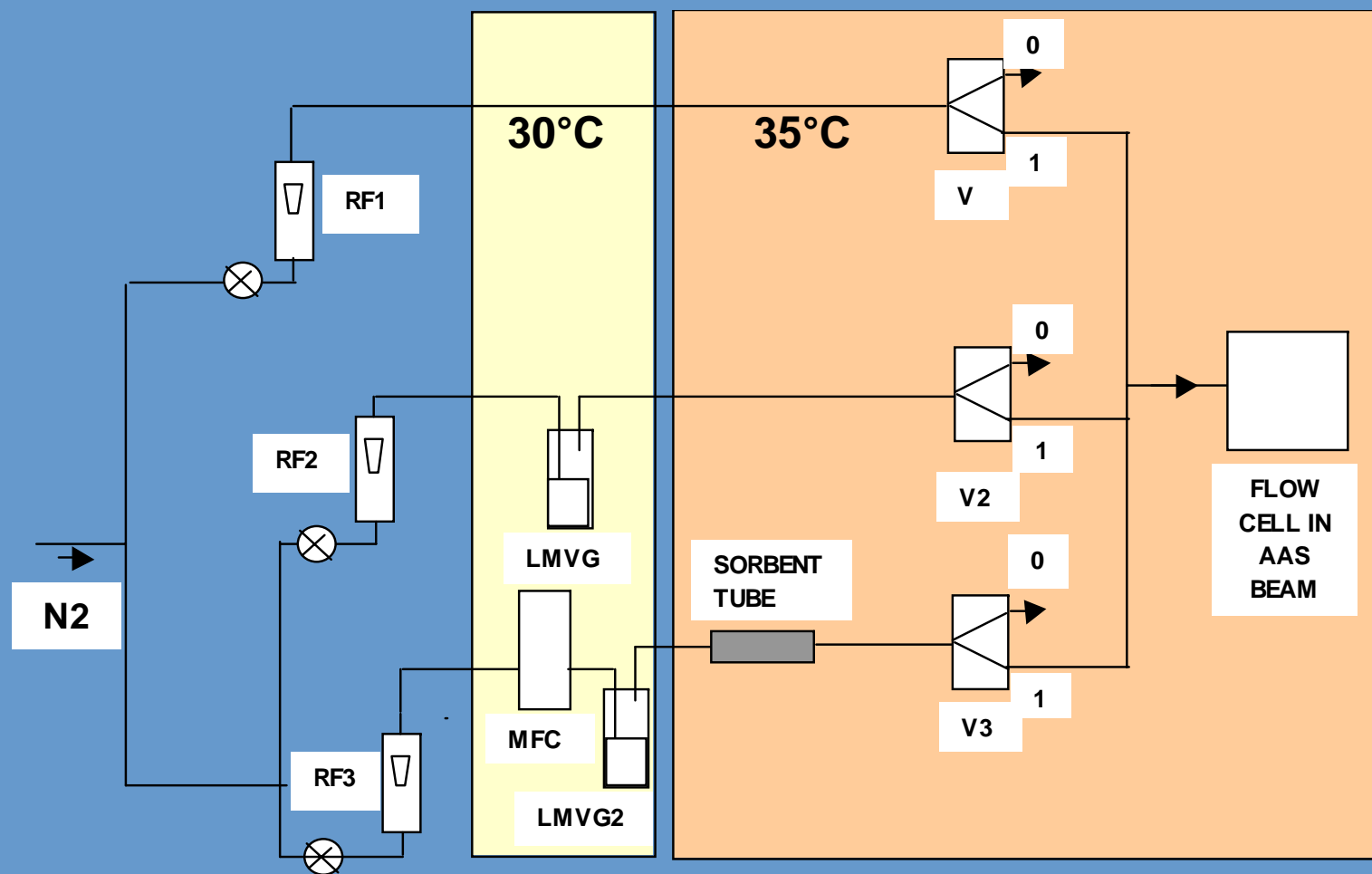


# Hg test facility for screening adsorbents



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## Arrangement of gas flow paths through the rig

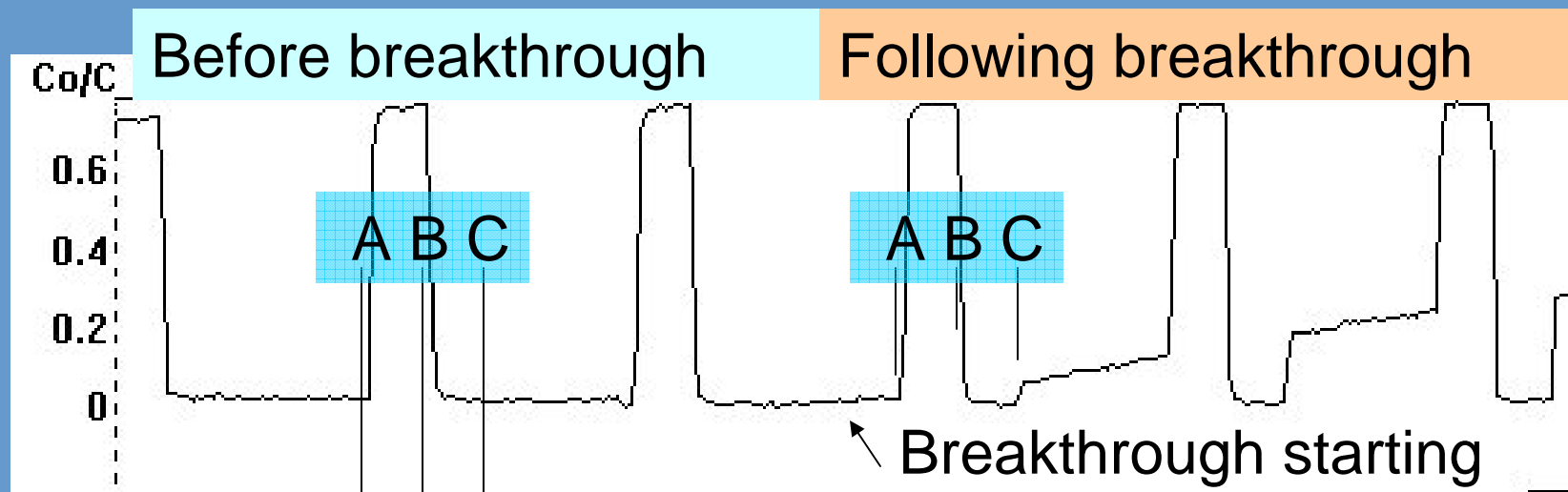






## Current version of test rig

- sorbent bed 50 mm long x 6 mm diameter
- saturated Hg vapour in 80ml/min N<sub>2</sub> flow through adsorption tube (controlled by mass flow controller)
- vapour generators maintained at 30 – 31°C
- sorbent tube and all downstream pipework at 35°C
- Facility upgraded for studying Hg adsorption at higher temperatures (e.g. 300°C) or the effects of acid gas species, moisture and oxygen on sorbent behaviour



Time →

**C** V3 open for 90 s - tube outlet Hg signal

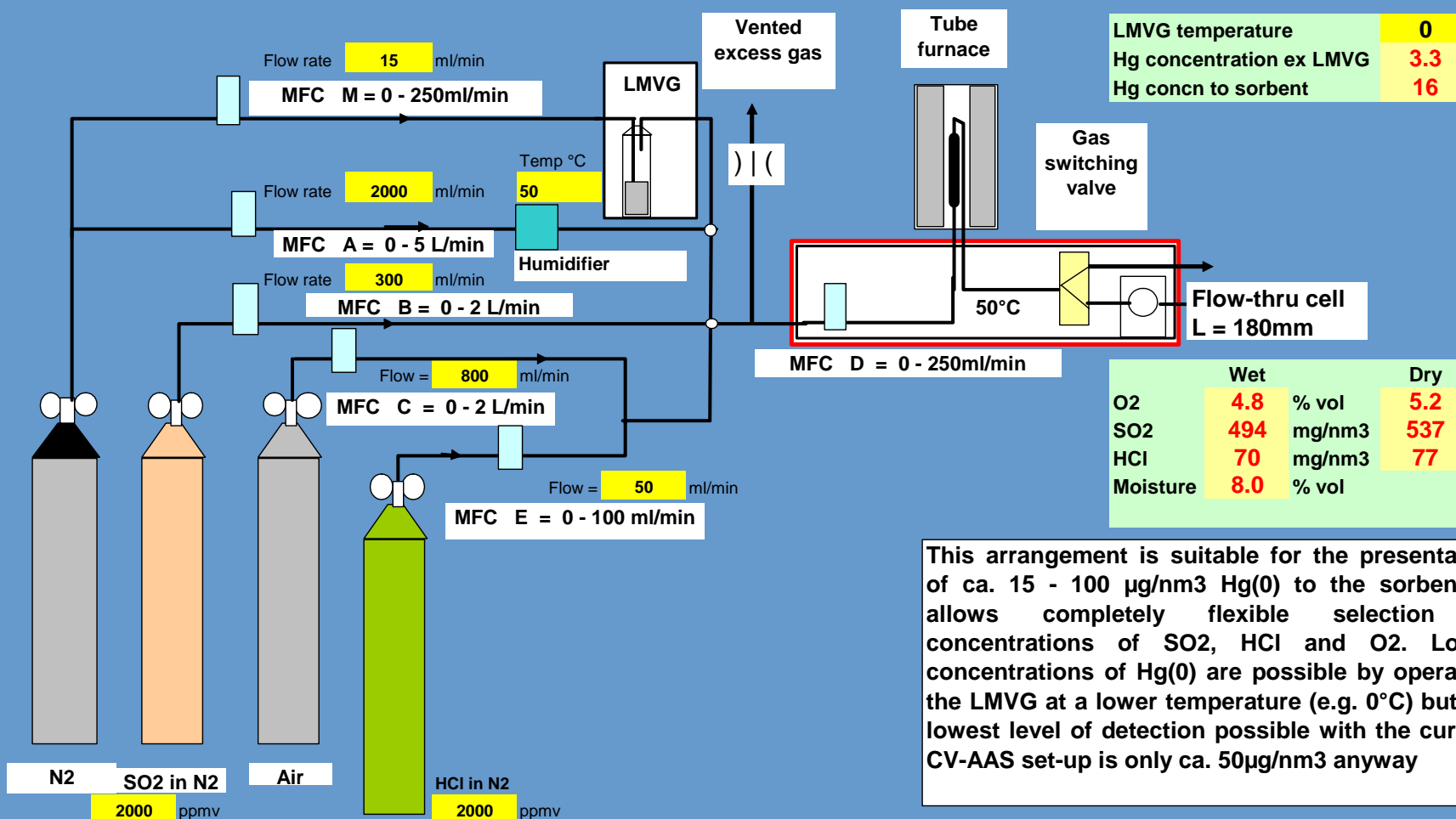
**B** V1 open for 90 s - nitrogen ('zero' gas) signal

**A** V2 open for 240 s - tube inlet signal

# Modifications to adsorption rig



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# Effect of sorbent dilution on mass loading and breakthrough time



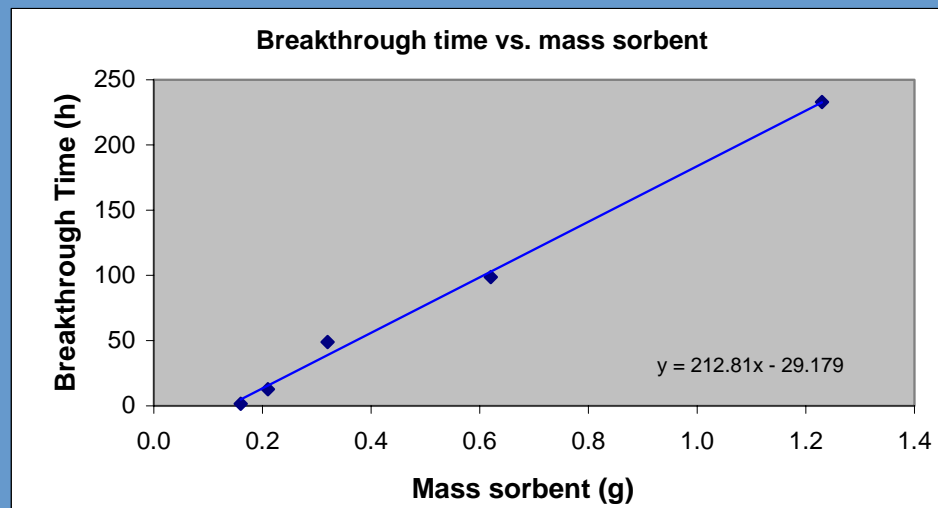
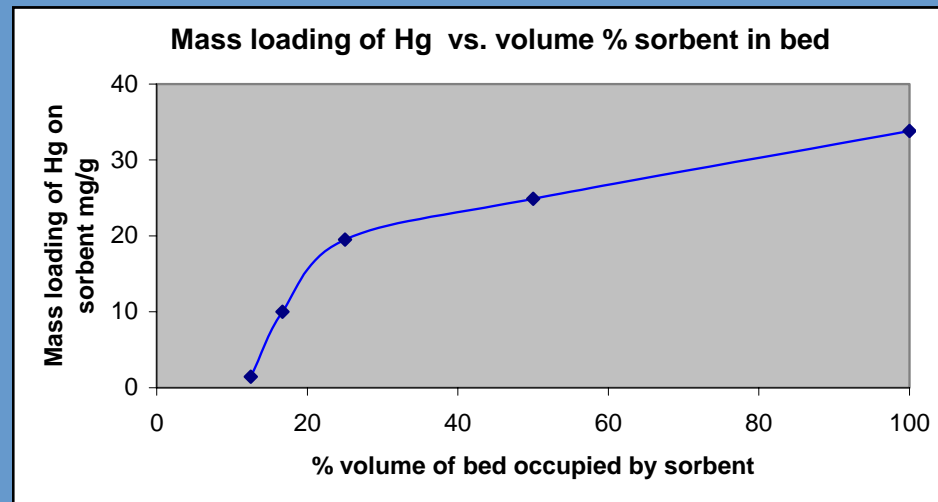
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Ratio of sorbent to sand (by volume)	% of sorbent in bed (by volume)	Mass of sorbent 705/1 g	Break-through time h	Mass loading of Hg mg/g
1 : 7	12.5	0.16	1.45	1.44
1 : 5	16.7	0.21	12.60	10
1 : 3	25	0.32	49.00	19.5
1 : 1	50	0.62	98.60	24.9
-	100	1.23	233.00	33.8

## Standard conditions

Bed dimensions 5 cm x 6 mm  
Hg inlet concn ca.34 mg/nm<sup>3</sup>  
N<sub>2</sub> carrier flow 80 ml/min

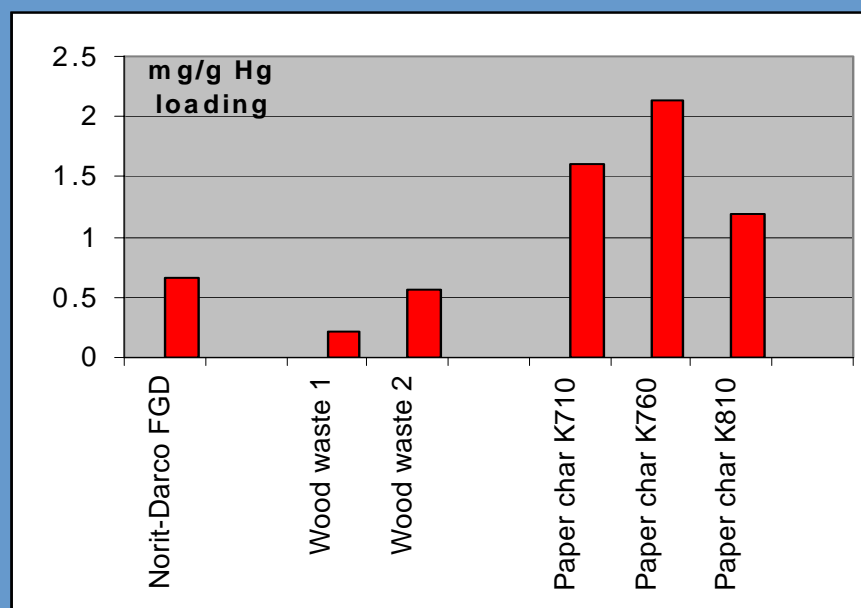
Sorbent temperature 35°C



# Sorbent development: Comparison of CFB gasifier chars-1



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Sorbent (all undiluted)	Mass sorbent g	Break-through time h	Break-through mass loading mg/g
Norit-Darco FGD carbon	0.56	2.3	0.67
ECN Petten CFB gasifier char - wood waste feedstock, test 1	0.38	0.51 †	0.21
ECN Petten CFB gasifier char - wood waste feedstock, test 2	0.46	1.64	0.56
ECN Petten CFB gasifier char - paper waste feedstock, K710	0.59	5.25	1.6
ECN Petten CFB gasifier char - paper waste feedstock, K760	0.61	8.5	2.13
ECN Petten CFB gasifier char - paper waste feedstock, K810	0.62	4.8	1.19

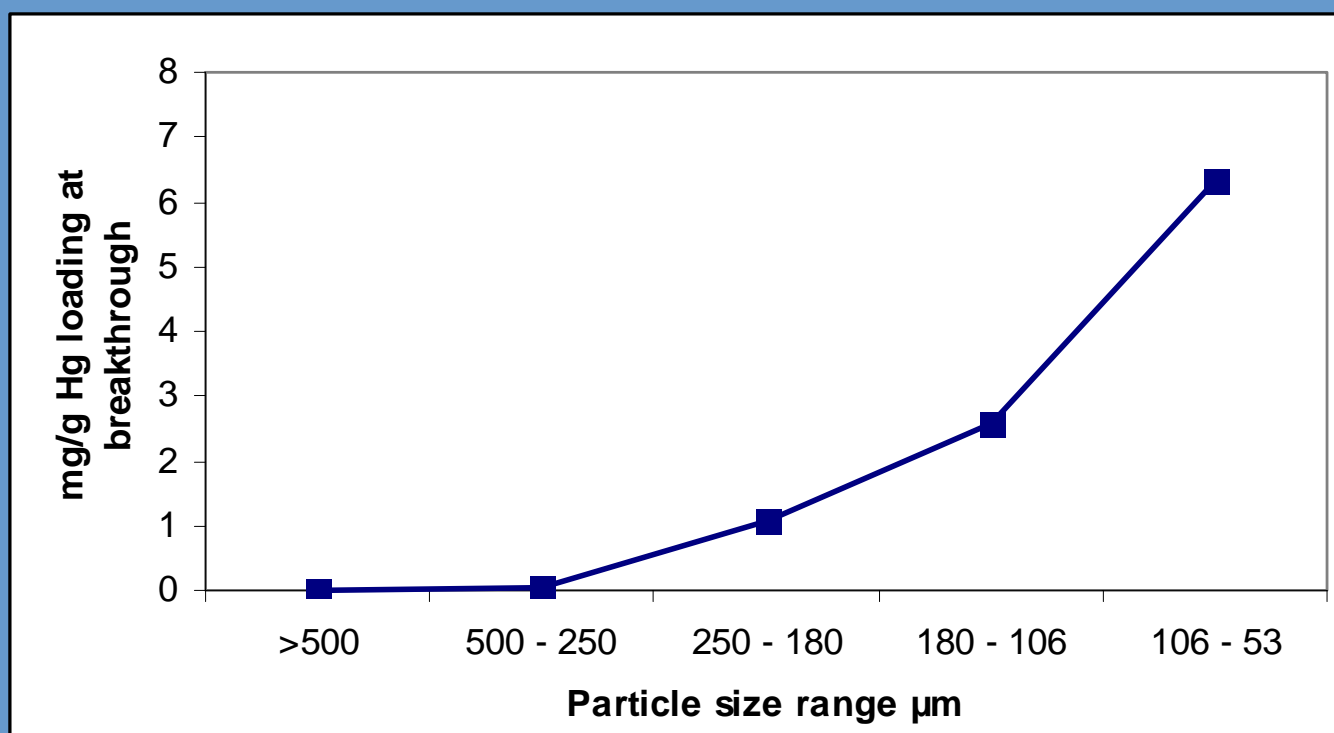
# Sorbent development: Comparison of CFB gasifier chars-2



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## Effect of particle size on Hg uptake

*CFB gasification char –paper waste*



### Standard conditions

Bed dimensions 5 cm x 6 mm; Hg inlet concn *ca.* 34 mg/nm<sup>3</sup>; N<sub>2</sub> carrier flow 80 ml/min

Sorbent temperature 35°C

# Sorbents supported



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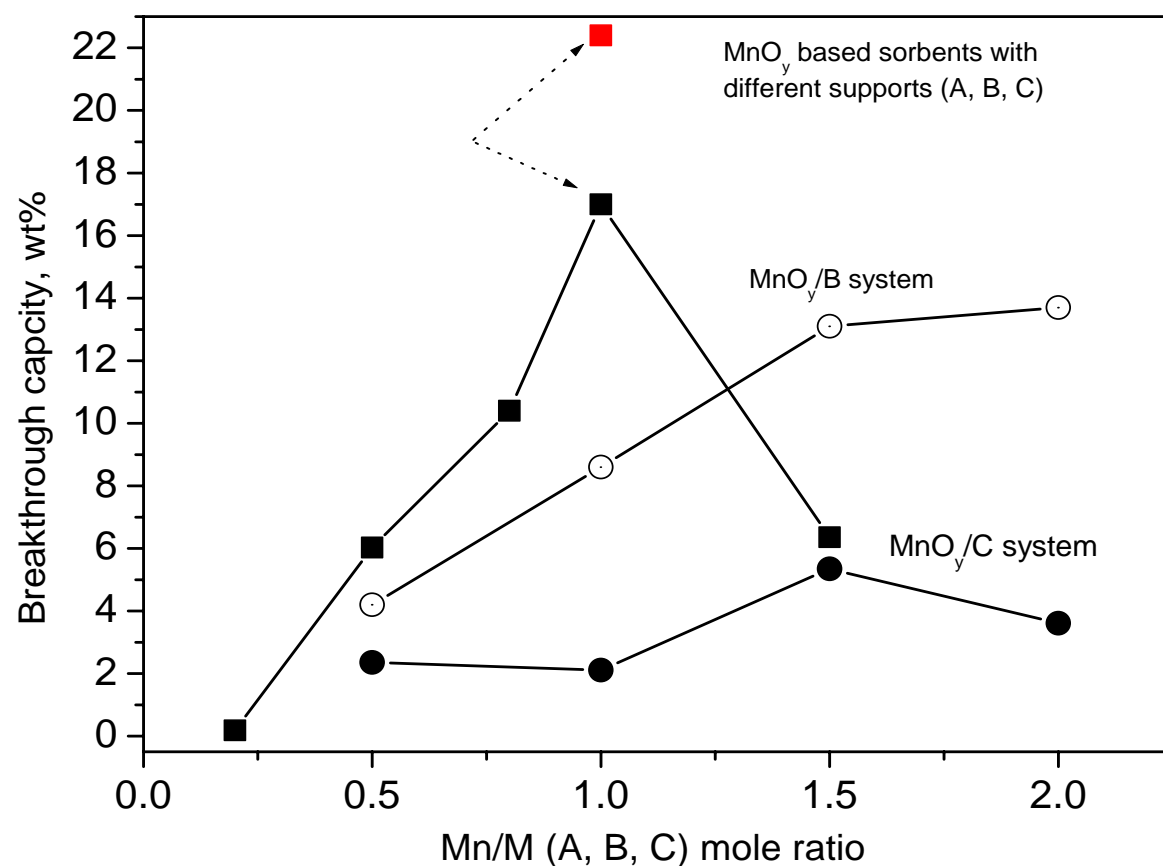


# Sorbent development: Inorganic sorbents-1



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## Summary of breakthrough capacities for “MnO<sub>2</sub>” – base sorbents as a function of composition



### Sorbent test

**conditions:** Hg  
evaporation chamber:  
30°C;  
Test chamber: 35°C;  
N<sub>2</sub> flow: 80 ml/min;  
Sorbent bed: 5 cm x 0.5  
cm i.d.; dilution factor: 3  
(sand/sorbent by  
volume)

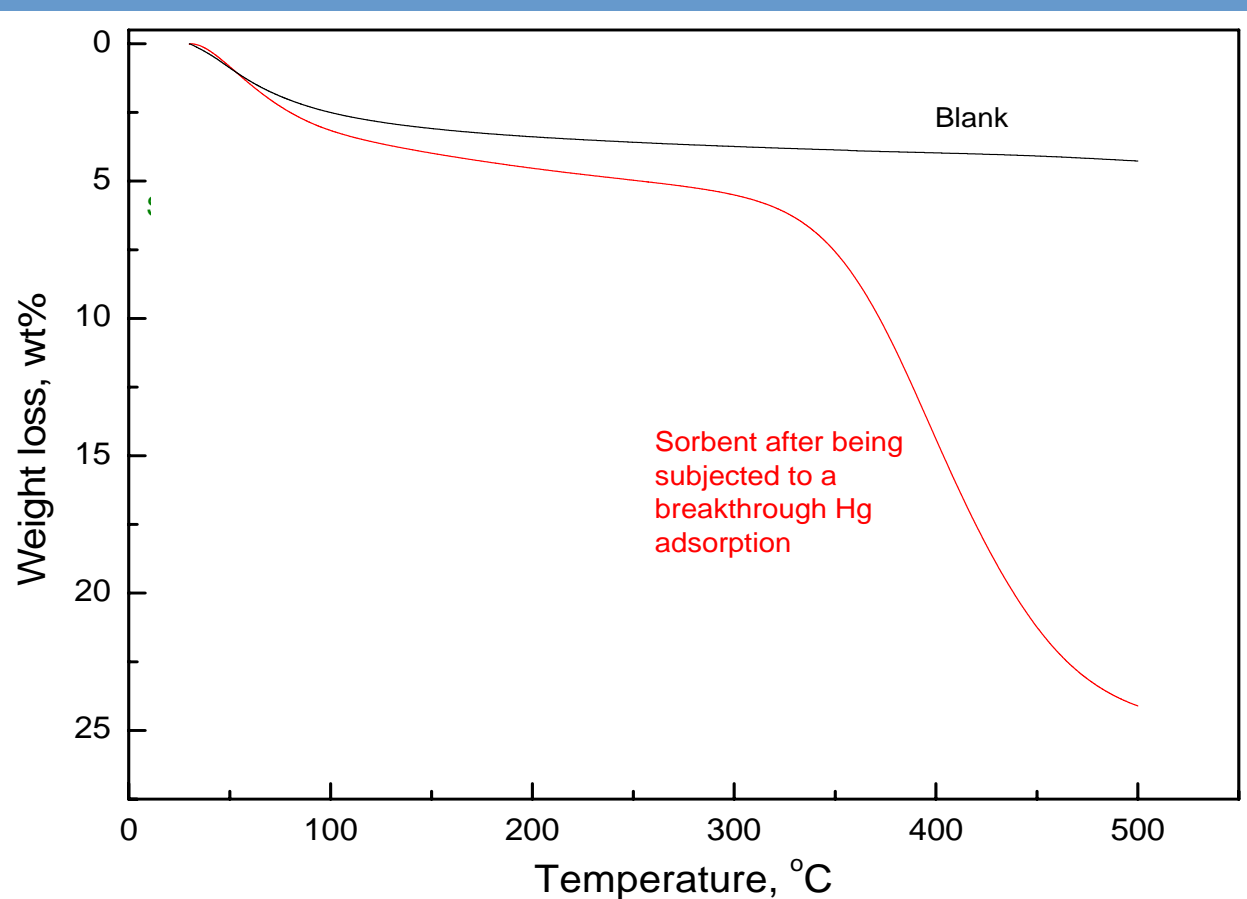
■ Capacity achieved for  
bed packed solely with  
sorbent at a temperature  
of 50°C and a N<sub>2</sub> flow of  
130 ml/min.

# Sorbent development: Inorganic sorbents-2



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Weight loss from  $\text{MnO}_2$  adsorbent containing 22% w/w Hg



Most of Hg adsorption capacity retained until 300°C and then steady decrease to 500°C.

# Sorbent development: Inorganic sorbents-3

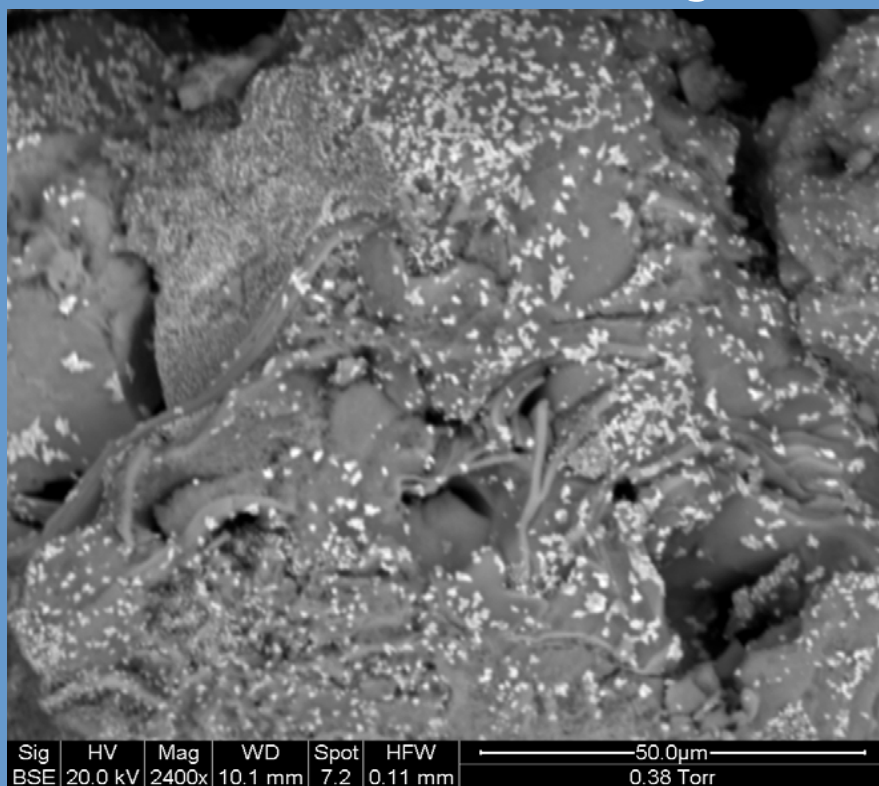


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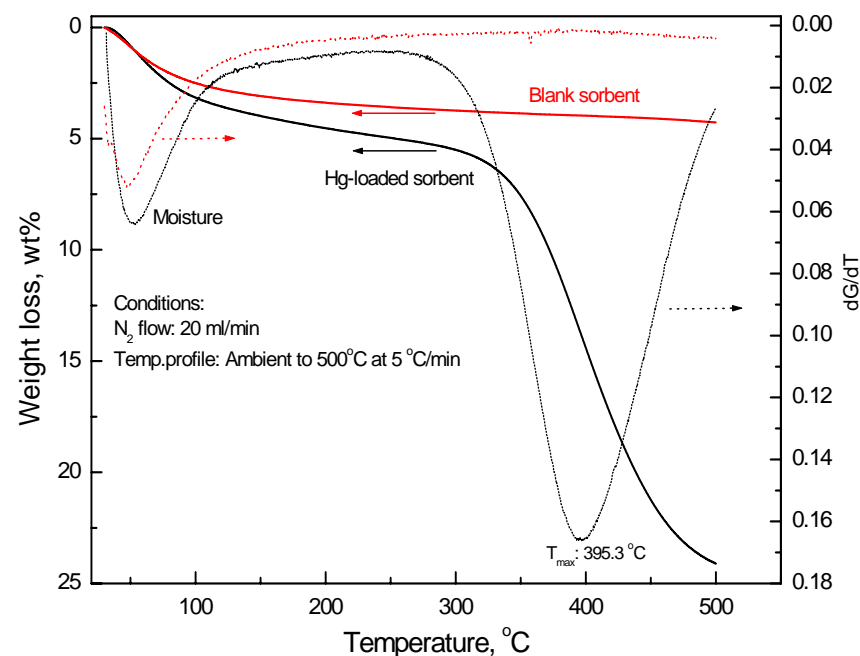
## SEM & TGA Analysis

*Chemical, as opposed to physical, adsorption  
dominates mercury uptake by the sorbent*

Hg distribution on sorbent  
surface at breakthrough



Very little desorption occurs at  
temperatures below 300 °C



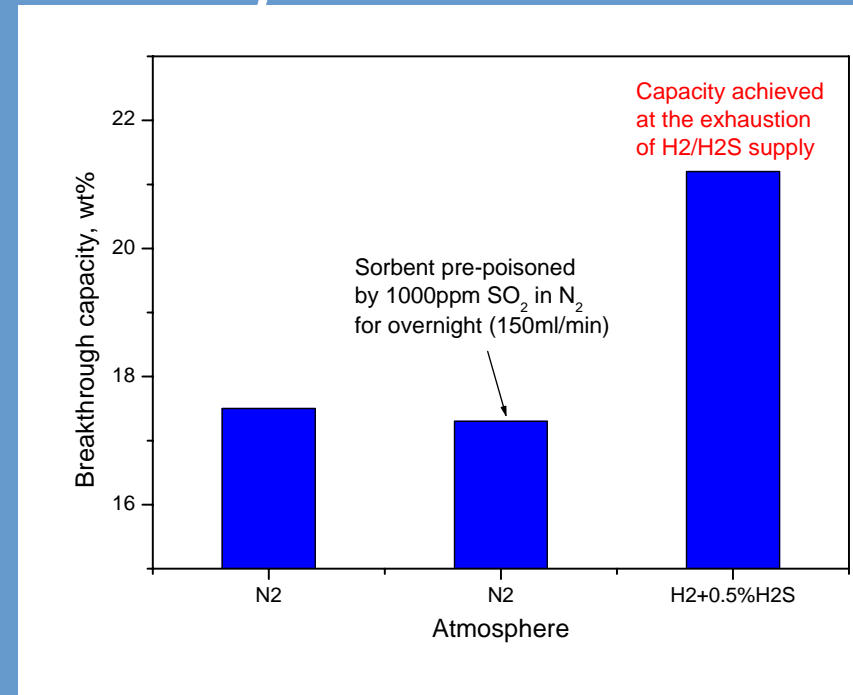
# Sorbent development: Inorganic sorbents-4



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## Sorbent or Catalyst? *Uncompromised performance against poisoning species in different atmospheres*

1. No obvious effect was found of the  $\text{SO}_2$  pre-poisoning treatment on the sorbent performance, though further tests being conducted using  $\text{N}_2/\text{SO}_2$ .
2. In the presence of  $\text{H}_2\text{S}$ , the sorbent behaves more like a catalyst, converting all Hg into  $\text{HgS}$ . The  $\text{HgS}$  appears to be easily carried away by the flowing gas stream, rather than deposit onto the sorbent surface, blocking the surface porosity.
3. A capacity of 21.3 wt% was achieved at the exhaustion of  $\text{H}_2/\text{H}_2\text{S}$  mixture, still without any sign of Hg breaking through.



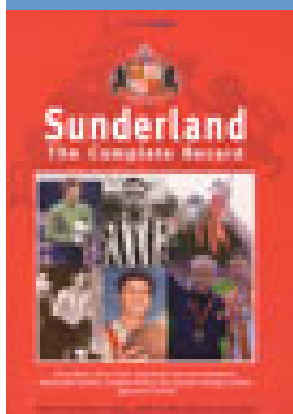
**Test conditions:** Sorbent/sand ratio: 3; Gas flow: 80~100ml/min; Temperature: 30 °C; Bed dimension: 0.5cm(id) x 5 cm



# Sorbent development: Inorganic sorbents- A winner?



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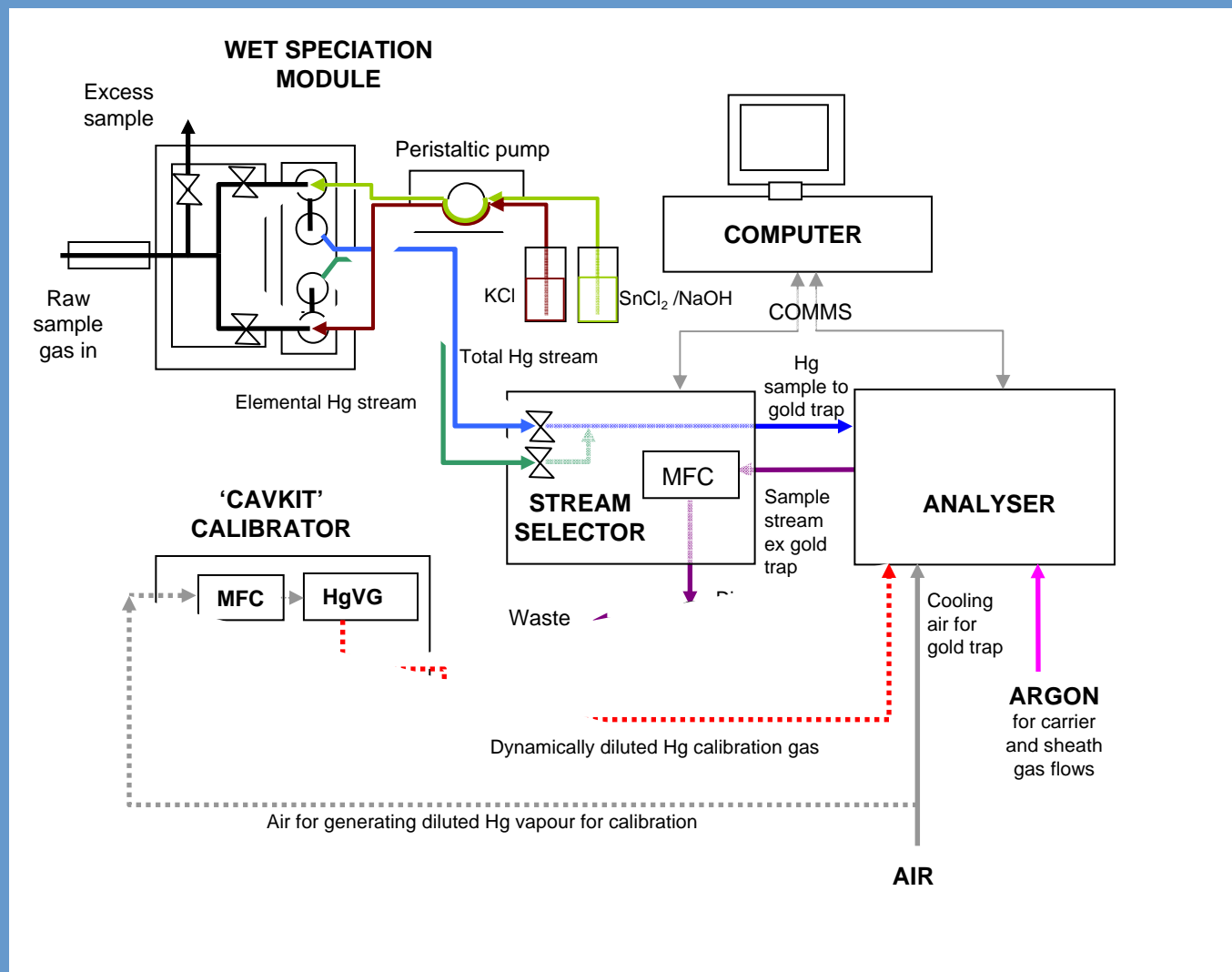


1973 FA. Cup Winners

# Sorbent testing capabilities



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# Sorbent testing capabilities



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# Properties of fly ash that affect mercury capacity-1

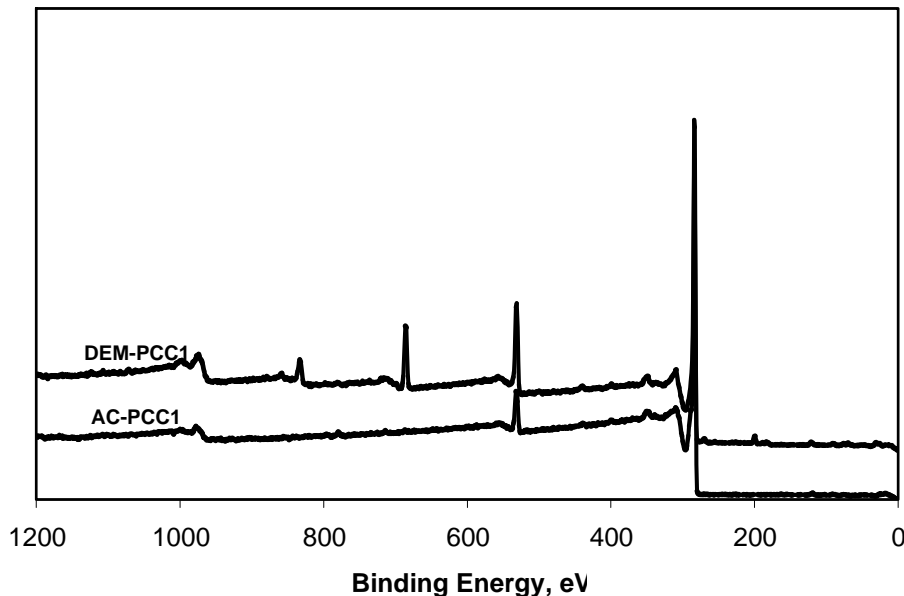


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Sample	Ash Content %	$S_{\text{BET}}$ $\text{m}^2/\text{g}$	$V_{0.95}$ $\text{ml/g}$	$D_a$ $\text{nm}$	Mercury capacity $\text{mg/g}^*$
FA1-Dem	3.6	53	0.040	3.0	1.85
AC-FA1	11.2	863	0.490	2.3	0.23
Darco Insul.	-	700	-	-	2.77

Note: Darco Insul is a byproduct of Darco FGD.

\* Tested using a fixed bed at 138°C using a simulated flue gas



Oxygen functionality of fly ash carbons plays an important role during mercury adsorption, while the surface area does not seem to have a significant impact on its mercury capacity.

Maroto-Valer et al., *Fuel*, **2005**, 84

# Properties of fly ash that affect mercury capacity-2

Sample	T (breakthrough), hr	Hg loading, mg Hg/g
A1	45.79	7.30
FGL	19.78	3.00
FA2	16.80	2.62
FA1	15.88	2.50
FGD	10.46	1.40
Gasif-1	0.27	0.023
Gasif-2	0.12	0.011
CPC-Knockout	0.04	Not determined
DarkAsh00	immediate	none
DarkAsh99	immediate	none
F9830	immediate	none
Tra-WoodFA	immediate	none
CPC-Filter	immediate	none

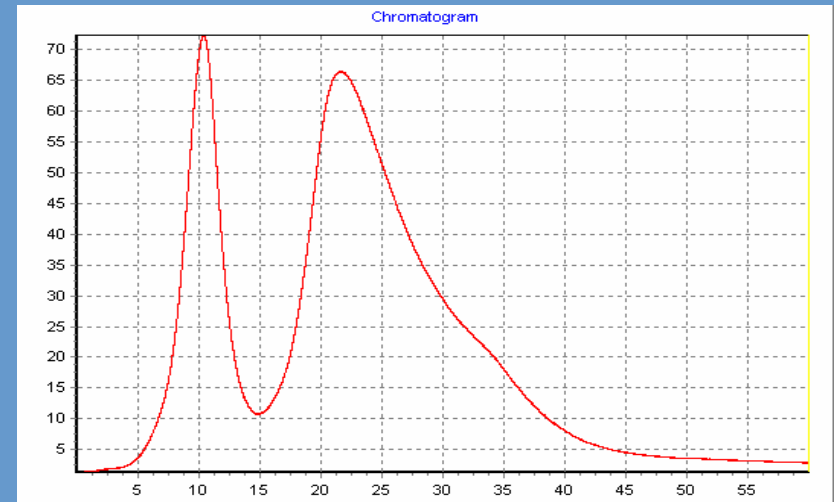
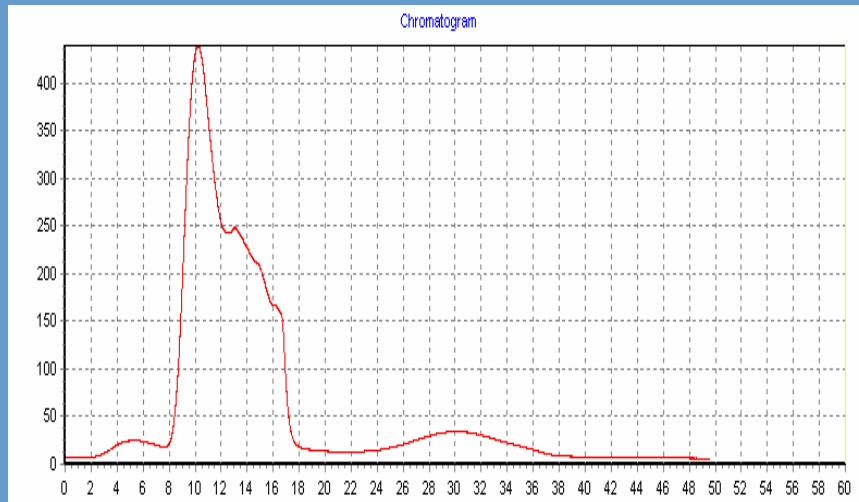
The physico-chemical properties of a suite of fly ash samples are analyzed and related to their ability to capture mercury vapor.



# Properties of fly ash that affect mercury capacity-3

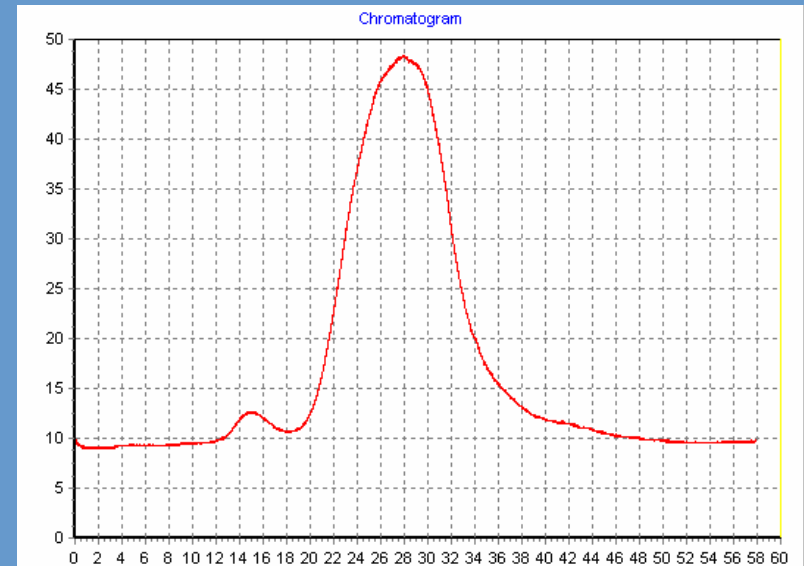


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Mercury speciation in solid samples by thermal decomposition and AFS:

- Identification and quantification of mercury species
- PSA Thermogram coupled with a Milenium Merlin



# Conclusions



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- Mercury is a hazardous air pollutant and coal utility boilers are the largest source of anthropogenic mercury emissions
- Mercury control regulations are being developed
- Regulatory and compliance strategies are being developed
- No single control technology can provide efficient and economical control for all power plants
- Significant advances will depend on the understanding of mercury chemistry (oxidation and capture)

# Acknowledgements

The authors would like to thank past and current collaborators and sponsors for their support.



*Colin, Congratulations!*



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